

# PATENT SPECIFICATION

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#### (54) DETERGENT COMPOSITION

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, EC4, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to detergent compositions having an improved anti-yellowing and anti-ashing activity.

The washing and cleaning of textile materials is known to be governed by two important factors, i.e. the removal of soil from the textile materials and the suspending of the removed soil in the wash liquor. If the detergent composition lacks sufficient soil-suspending power, the soil is redeposited from the wash liquor on the textile materials, which on repeated washing results in an increasing yellowing of these materials. The soil normally consists of a mixture of organic and inorganic materials, the latter being determined by ashing of the soiled textile materials. The residue obtained by this ashing is generally called ash, which frequently consists of insoluble calcium salts. During the washing operation these calcium salts can be formed by the hardness salts of the water used, and if the detergent lacks sufficient soil-suspending power, they may be deposited on the textile materials and thus result in an unacceptable incrustation of the textile materials, imparting an unpleasant "grip" to the washed textiles.

35 In order to keep the soil suspended in the wash liquor and to reduce the formation of insoluble calcium salts, the washing industry has long been using builders, among which the condensed phosphates, particularly sodium polyphosphate, are most commonly used. Attention has lately been drawn to the possible contribution of the condensed phosphates to the eutrophication of lake and river waters and numerous suggestions have been made to reduce the content of the condensed phosphates in detergents by wholly or partly replacing these phosphates by other complexing compounds.

A reduction of the phosphate content however in most cases results in a decreased soil-suspending power, which has then to be compensated again by the incorporation of particular additives.

Such an additive has e.g. been disclosed in German Patent Specification No. 1,945,702. According to this publication the addition of ethylene diamine tetramethylene phosphonic acid or its salts to a phosphate containing detergent composition results in an improved soil-suspending power, thus preventing the redeposition of soil on textiles in the aqueous solutions. Another proposal, made in German Patent Specification 1,926,027, involves the addition to detergent compositions which contain a mixture of sodium tripolyphosphate and sodium nitrilotriacetate as builders, of from 0.25—3 per cent of a soil-suspending agent consisting of a combination of a cellulose ether and a gelatin protein. These additives however do not always give an entirely sufficient improvement in soil-suspending power, or in other words, the reduction in yellowing and ashing obtained is insufficient.

The present invention now provides a solution for the problem of improving the anti-yellowing and anti-ashing activity of detergent compositions, particularly of detergent compositions having a reduced phosphate content, consisting in the incorporation into the detergent compositions of a combination of certain complexing compounds and certain protective colloids. It has been found that the activity obtained by this combination cannot be achieved by the addition of the individual components. The present invention provides therefore a detergent composition having an improved anti-yellowing and anti-ashing activity comprising one or more detergent active compounds and one or more phosphate builder salts, characterised in that the detergent composition comprises from 1—10% by weight of one or more calcium complexing compounds with a  $pK_{Ca}^{+ +}$  of 5—9.5 selected from organic phosphonic acids and substituted polyacrylic acids and their sodium, potassium and ammonium salts, and from

5	0.05—10% by weight of one or more protective colloids selected from polyvinylpyrrolidones, alkylpolyvinylpyrrolidones, polyvinylpyrrolidone/vinyl acetate copolymers, casein, caseinate and gelatin.	be used in admixture with each other according to the invention.	65
10	The specific complexing compounds according to the invention are $\text{Ca}^{++}$ -sequestering organic compounds selected from the group of organic phosphonic acids and substituted polyacrylic acids and their sodium, potassium and ammonium salts. These compounds have a calcium complexing constant in the range of 5—9.5. Particularly suitable organic phosphonic acids and phosphonates are the following: 1-ethane-hydroxy-1,1-diphosphonic acid, nitrilo trimethylene phosphonic acid and ethylene diamine tetramethylene phosphonic acid and their sodium, potassium and ammonium salts.	The complexing compounds of the invention are generally used in the detergent compositions in an amount of 1—10% by weight. The lower the phosphate content of the detergent, the higher the content of complexing compounds. At a total phosphate content of e.g. 20, 25 and 30% by weight, respectively, the content of complexing agents according to the invention is about 4—10%, about 3—7% and 2—6%, respectively. The protective colloids are used according to the invention in an amount of 0.05—10%, particularly 0.1—5% by weight, calculated on the detergent composition.	70
15		The weight ratio of the complexing compound to the protective colloid in the combination according to the invention is generally from 100:1 to 1:2, preferably from 50:1 to 2:1.	75
20	Suitable substituted polyacrylic acids are poly-alpha-hydroxy-acrylic acids having a polymerisation degree of at least 3. The COOH:OH ratio, that is the ratio of the number of carboxyl groups to the number of hydroxyl groups in these compounds generally lies between 1:2 and 3:1, the ratio of 1:1 being preferred. The molecular weight is at least 261, and generally varies between about 800 and 30,000. These poly-alpha-hydroxyacrylic acids can also be applied in the form of their sodium, potassium and ammonium salts, and they may also be formed during the manufacture of the detergent composition by hydrolysis of the corresponding lactones with available alkali.	The combination according to the invention is used in detergent compositions containing a synthetic detergent or a soap or mixtures thereof, together with the additives and adjuvants normally used in detergent compositions. Soap includes an alkalinetal, e.g. Na- or K-salt of a $\text{C}_{10}$ — $\text{C}_{24}$ fatty acid.	80
25		The detergent compositions essentially include one or more anionic, nonionic, amphoteric or zwitterionic detergent active compounds, or mixtures thereof, and builder salts.	85
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50			110
55			115
60			120
			125

(C<sub>6</sub>—C<sub>20</sub>) with sodium bisulphite and those derived by reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> or O<sub>2</sub>, followed by hydrolysing with a base to produce a mixed sulphonate; and olefin sulphonates, which term is used to cover the material made by reacting olefins, particularly alpha-olefins, with SO<sub>3</sub> and then neutralising and hydrolysing the reaction product.

Nonionic detergent active compounds may also be used. Examples include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C<sub>6</sub>—C<sub>12</sub>) phenols, generally 5 to 25 EO (EO=ethylene oxide unit); i.e. 5 to 25 ethylene oxide units per molecule. Further examples are the condensation products of aliphatic (C<sub>8</sub>—C<sub>18</sub>) alcohols and fatty acid amides with ethylene oxide, generally 6 to 30 EO units, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other nonionic detergent active compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent active compounds, for example mixed anionic or mixed anionic and nonionic compounds may be used in the detergent compositions, particularly to impart controlled low sudsing properties thereto. This is particularly beneficial for compositions intended for use in suds-intolerant, automatic washing machines. Mixtures of amine oxides and ethoxylated nonionic compounds may also be beneficial.

Many suitable detergent active compounds are commercially available and are described in the literature, for example in "Surface Active Agents and Detergents" by Schwartz, Perry and Berch.

Amounts of amphoteric or zwitterionic detergent active compounds can also be used in the compositions of the invention but this is not normally desirable owing to their relatively high cost. If any amphoteric or zwitterionic detergent active compounds are used, it is generally done in small amounts in compositions based on the much more commonly used anionic or nonionic detergent active compounds.

The amount of the synthetic detergent active compound or compounds used is generally in the range of from 5% to 50%, preferably 15% to 30%, by weight of the compositions, depending on the desired properties. The detergents also contain builder salts. The ratio by weight of the builder salts to the detergent active compounds ranges generally from about 1:20 to about 20:1, preferably about 1:3 to 10:1, especially from about 1:1 to about 5:1. Examples of these builder salts are tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphate, trisodium and tripotassium nitrilotriacetate, ether polycarboxylates such as sodium glycolate-malonate, citrates, oxidised starch and cellulose derivatives, especially those containing dicarboxyl radicals, sodium alkenyl (C<sub>10</sub>—C<sub>20</sub>) succinates, sodium sulpho-fatty acids, alkali metal carbonates and orthophosphates and polyelectrolyte builders such as sodium copolyethylene-maleate. The preferred builder salts are the condensed phosphates, particularly sodium tripolyphosphate, which can be partly replaced by one or more of the above-mentioned builder salts. The present invention relates in particular to detergent compositions of which the phosphate content is not sufficient to effect a complete complexing of the hardness salts of the wash liquor used, i.e. detergent compositions having a reduced phosphate content, e.g. 15—30 per cent by weight.

Other conventional materials may be present in the detergent compositions of the invention, for example supplementary soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers, optical brighteners, enzymes, suds boosters, suds depressants, germicides, anti-tarnishing agents, cationic detergents, fabric softening agents, chlorine-releasing agents, oxygen-liberating bleaches such as sodium perborate or percarbonate with or without bleach precursors, buffers and the like. The balance of the detergent compositions is water, for example in the range of from 5 to 15% in the powdered detergent compositions.

The detergent compositions of the present invention may be in any of the usual physical forms for such compositions, such as powders, beads, flakes, bars, tablets, noodles, liquids and pastes. The detergent compositions are prepared and utilised in the conventional manner, for example in the case of powdered detergent compositions they may be made by spray-drying aqueous slurries of the detergent ingredients or by dry-mixing processes.

The invention is further illustrated by means of the following Examples. The tests were carried out under the following test conditions in an Atlas-Launderometer:

Dosing of the detergent composition: : 6 g/litre  
 Cloth/liquor ratio : 1:25  
 Water : 23° DH  
 Test fabric : Krefeld Standard  
 Test cloth EMPA 101  
 Washing time : 35 min up to 95° C;  
 10 min at 95° C.  
 Number of washings : 10

Dosing of the detergent composition:	: 6 g/litre
Cloth/liquor ratio	: 1:25
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Washing time	: 35 min up to 95° C; 10 min at 95° C.
Number of washings	: 10

5 All percentages given in the Examples are by weight.

5 In these experiments a detergent base formulation of the following composition was used (the perborate was separately added to the formulation):

	%
sodium alkyl benzene sulphonate	6
nonyl phenol 10 EO	4
10 Na-tallow fatty acid soap	2
sodium tripolyphosphate	30
sodium pyro and orthophosphate	8
sodium silicate	4
15 sodium carboxy methylcellulose	0.8
sodium sulphate	2
sodium perborate	30
perfume, optical brighteners, suds controllers, etc.	4.7
water	8.5

20 The dosing applied was calculated on a theoretical product having 20% instead of 38% total phosphate; consequently, the dosing involved

$$20 \\ 0.7 \times 6 \times \frac{—}{38} \text{ g/l}$$

phosphate and  $0.3 \times 6 \text{ g/l}$  sodium perborate. This formed the base formulation containing 20% sodium polyphosphate; for the experiments with 25% and 30%, respectively, only  $0.05 \times 6 \text{ g/l}$  and  $0.1 \times 6 \text{ g/l}$  were added, respectively. This ensured that all substances, except the tripolyphosphate, were present in the same amount in all experiments.

25 In Example IA, however, the base formulation was prepared by means of separate weighings. In Example IB the base formulation was obtained as spray-powder.

30 The ashing was measured as the difference in reflection (DR) by means of an Elrephometer. The ash was determined by ashing and gravimetric titration.

40

#### EXAMPLE I.

A. Several combinations of ethylene diamine tetramethylene phosphonic acid (Dequest® 2041 ex Monsanto Dequest is a registered trade mark) and gelatin (ex Merck) were tested in the base formulation with different sodium tripolyphosphate concentrations, as regards yellowing and ash, and compared with the base formulations without the combinations or with only one of the components of the combinations. The following results were obtained:

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Additive	Base formulation having a sodium tripolyphosphate content of:							
	15%				20%			
Dequest® 2041 (%)	—	5	—	5	—	5	—	5
Gelatin (%)	—	—	5	5	—	—	5	5
Yellowing (DR)	24.6	10.6	14.4	5.2	20.4	11.2	18	3.8
Ash (%)	4.1	0.6	4.6	1.1	5.3	0.2	5.2	0.1
Dequest® 2041 (%)	25%							
	—	5	—	5	—	5	—	5
	—	—	5	5	—	—	5	5
	16.4	10.4	15.4	2.6	8.6	13.8	6	3
Ash (%)	5.1	0.1	5.4	0.1	2.2	0.1	2.9	0.1

B., On using the base formulation, not prepared by separate weighings, the following results were obtained by varying the contents of Dequest and/or gelatin, respectively:

	Base formulation having sodium tripolyphosphate content of:									
	20%					25%				
	Dequest (R) 2041	5	5	2	2	-	5	5	2	-
Gelatin (%)		5	2	2	5	-	5	2	2	-
Yellowing (DR)		5.6	3.8	25.2	28.2	22	3.6	4.0	22.2	22.6
Ash		0.2	0.2	4.3	4.2	5.0	0.1	0.1	2.3	2.5
										29.4

C. For comparison, Example IA was repeated with a formulation of 5% sodium nitrilotriacetate (NTA) and 5% gelatin, with the following results:

	Base formulation having an STP content of:			
	15%		20%	
	25%	30%		
NTA	5	5	5	5
Gelatin	5	5	5	5
Yellowing (DR)	16.6	10.8	2.4	5.4
Ash (%)	4.2	0.4	0.2	0.2

## EXAMPLE II

Example IB was repeated, except that the amounts of Dequest (R) 2041 and gelatin were varied. The following results were obtained, at an STP content of 20% 25% respectively (a and b):

Dequest 2041 (%)	5	5	5	5	4	4	4	3	3	3	2	2
Gelatin (%)	5	2	1	0.5	2	1	0.5	2	1	0.5	5	2
Yellowing	5.6	3.8	4.6	4.6	6.2	6.2	5.2	16.6	26	16	28.2	25.2
Ash	0.2	0.2	0.2	0.2	0.9	0.5	0.7	2.7	3.1	2.4	4.2	4.3
Yellowing	3.6	4.0	3.6	5.0	4.2	3.0	3.8	4.6	5.0	7.0	22.6	22.2
Ash	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.3	0.5	0.6	2.5	2.3

At an STP content of 30% the following results were obtained:

Dequest 2041 (%)	—	0.5	0.5	0.5	1	1	1	2	2	2
Gelatin (%)	—	—	0.25	0.5	—	0.25	0.5	—	0.25	0.5
Yellowing	28.4	32.4	25.8	25.2	26.8	24.4	23.6	14.4	16.0	9.6
Ash	3.6	2.6	2.8	2.9	1.8	1.6	1.7	0.3	0.3	0.2

### EXAMPLE III

Example IB was repeated, with various combinations of poly-alpha-oxyacrylic acid (ex Knapsack, having a COOH/OH-ratio of 1:1) and gelatin, at an STP content in the base formulation of 20, 25 and 30%, respectively (a, b and c).

Poly-alpha-oxyacrylic acid (%)	5	5	3	3	2	2
Gelatin	—	2	—	2	—	0.5
Yellowing	26.4	7.2	23.4	15.8	—	—
Ash	1.9	1.4	3.5	3.1	—	—
a	11.4	5.4	25.0	21.8	—	—
b						
c	1.1	1.4	3.5	3.8	—	—
	13.0	3.8	10.2	4.0	10.6	6.2
	0.2	0.1	0.6	0.5	1.2	1.3

EXAMPLE IV

Combinations of Dequest 2041 or poly-alpha-oxyacrylic acid with casein ex Merck were tested as in Example 1B.

The following yellowing and ashing values were found:

	20% STP					
	Dequest 2041 (%)	Poly-alpha-oxyacrylic acid (%)	Casein (%)	Yellowing	Ash	
Dequest 2041 (%)	—	—	4	4	—	—
Poly-alpha-oxyacrylic acid (%)	—	—	—	—	5	5
Casein (%)	0.5	2	0.5	2	0.5	2
Yellowing	40.4	39.0	14.0	6.6	13	12.8
Ash	4.7	4.5	0.7	0.9	1.8	1.9
	25% STP					
	Dequest 2041 (%)	Poly-alpha-oxyacrylic acid (%)	Casein (%)	Yellowing	Ash	
Dequest 2041 (%)	—	—	3	3	—	—
Poly-alpha-oxyacrylic acid (%)	—	—	—	—	4	4
Casein (%)	0.5	2	0.5	2	0.5	2
Yellowing	41.4	35.9	15.0	8.4	15.8	14.2
Ash	5.5	5.7	0.5	0.6	2.4	2.1
	30% STP					
	Dequest 2041 (%)	Poly-alpha-oxyacrylic acid (%)	Casein (%)	Yellowing	Ash	
Dequest 2041 (%)	—	—	2	2	—	—
Poly-alpha-oxyacrylic acid (%)	—	—	—	—	3	3
Casein (%)	0.5	2	0.5	2	0.5	2
Yellowing	38.9	35.7	14.6	9.0	6.0	3.0
Ash	3.9	3.8	0.6	0.5	0.6	0.9

EXAMPLE V.

On comparing the combination: 4% Dequest 2041 and 0.5% gelatin with combinations of 5 4% Dequest 2041 with 0.5, 2 or 5% of gum arabic, gum tragacanth or agar agar, according to Example 1B, the results showed in all cases that the yellowing of the combinations 10 which were not according to the invention was higher by about a factor 3, both for 20%

and for 25% total phosphate content.

EXAMPLE VI.

Mixtures of Dequest 2041 and poly-alpha-oxyacrylic acid or sodium polyhydroxyacrylate with gelatin or casein were tested as to yellowing and ash, as in Example 1B.

The following results were obtained:

	Total phosphate content 20%										
Dequest 2041 (%)	-	-	1	2	2	1	1	1	2	1	F.5
Poly-alpha-oxy-acrylic acid (%)	5	5	5	4	3	-	-	-	-	-	-
Sodium polyhydroxy acrylate (ex Solvay; (COOH/OH 1:1) (%)	-	-	-	-	-	5	4	5	5	6	4
Gelatin (%)	-	2	2	1	1	2	2	1	1	1	0.5
Yellowing	26.4	7.2	5.0	5.8	7.4	7.6	7.8	2.6	2.0	1.6	2.2
Ash	1.9	1.5	1.2	1.0	1.8	0.8	2.2	0.2	0.1	0.1	0.1

	Total phosphate content 25%		
Dequest 2041 (%)	1	1	1
Poly-alpha-oxyacrylic acid (%)	5	3	3
Gelatin (%)	2	1	0.5
Yellowing	4.0	4.6	6.4
Ash	0.3	1.4	1.5

	Total phosphate content 30%			
Dequest 2041 (%)	2	1.5	0.5	1
Poly-alpha-oxyacrylic acid (%)	1	1.5	3	2
Gelatin (%)	0.5	0.5	0.5	0.5
Yellowing	5.4	6.6	5.2	4.6
Ash	0.3	0.3	0.1	0.5

### EXAMPLE VII.

5 A combination of 5% and 4%, respectively, of ethane hydroxy diphosphonic acid (Turpinal

SL ex Henkel) and 5% of gelatin was tested as in Example 1B. The yellowing and ash values measured were:

	<u>5% Turpinal SL</u>	
	<u>Yellowing</u>	<u>Ash</u>
at a total phosphate content of 20%	0.8	0.1
at a total phosphate content of 25%	1.6	0.2
at a total phosphate content of 30%	3.8	0.5

  

	<u>4% Turpinal SL</u>	
	<u>Yellowing</u>	<u>Ash</u>
at a total phosphate content of 20%	5.8	0.2
at a total phosphate content of 25%	4.2	0.1
at a total phosphate content of 30%	4.0	0.1

5 A combination of 2.5% Dequest 2041, 2.5% Turpinal and 0.5% gelatin at a total phosphate content of 20% resulted in a yellowing value of 1.8 and an ash value of 0.2.

#### EXAMPLE VIII.

The experiment according to Example IB was repeated, but now at a temperature of 60° C. The following results were obtained:

	Total phosphate											
	20%			25%				30%				
	Dequest 2041 (%)	5	5	—	4	4	—	3	—	3	—	—
Polyhydroxyacrylate (ex Solvay) (%)	—	—	—	—	—	—	4	—	3	—	—	—
Gelatin (%)	—	2	0.5	—	2	0.5	2	2	2	0.5	—	—
Yellowing	15.4	8.8	8.2	16.6	8.4	9.2	7.4	9.0	8.0	7.8	19.6	—
Ash	4.3	0.2	0.1	3.9	0.2	0.2	0.5	0.1	0.1	0.1	2.4	—

#### EXAMPLE IX.

15 The experiments according to Example IB were repeated using as protective colloid either PVP (polyvinylpyrrolidone) having an average molecular weight of 10,000, or PVP/VA (polyvinylpyrrolidone/vinylacetate-copoly-

mer; VP/VA ratio 50/50; K-value in 1% ethanol solution 25—35, molecular weight abt. 40,000) in an amount of 0.01 and 0.25%, respectively, together with 5% Dequest 2041. The following results were obtained:

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	Total phosphate content	
	20%	
	Dequest 2041	5
PVP	0.1	—
PVP/VA	—	0.25
Yellowing	0.6	0.9
Ash	0.4	0.4

## EXAMPLE X.

The experiments according to Example IB were repeated, using however a composition with 20.8% STP. The dosage was calculated on a total phosphate content of 11%, i.e.

$$6 \times \frac{11}{20.8} \times 0.7 \text{ g/l}$$

phosphate— $6 \times 0.3 \text{ g/l}$  sodium perborate were involved. The higher total phosphate contents were achieved by separately adding STP, pyro- and orthophosphate, equivalent to the STP decomposition. The sequestrant used was Dequest 2041, and the protective colloid was gelatin.

10

The following results were obtained:

	Total phosphate content (in %)								
	11			14			17		20
	Dequest 2041 (%)	7.5	7.5	10	7.5	7.5	7.5	7.5	5
	Gelatin (%)	—	0.5	0.5	—	0.5	—	0.5	—
	Yellowing	4.9	3.8	0.8	12.7	1.2	2.5	0.5	3.8
	Ash	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
									2.4

## WHAT WE CLAIM IS:—

1. A detergent composition having an improved anti-yellowing and anti-ashing activity comprising one or more detergent active compounds and one or more phosphate builder salts, characterised in that the detergent composition comprises from 1—10% by weight of one or more calcium complexing compounds with a  $\text{pK}_{\text{Ca}^{++}}$  of 5—9.5 selected from organic phosphonic acids and substituted polyacrylic acids and their sodium, potassium and ammonium salts, and from 0.15—10% by weight of one or more protective colloids selected from polyvinylpyrrolidones, alkylpolyvinylpyrrolidones, polyvinylpyrrolidone/vinyl acetate copolymers, casein, caseinate and gelatin.
2. Detergent composition according to claim 1, in which the calcium complexing compound is ethane diamino tetramethylene phosphonic acid or its sodium, potassium or ammonium salt.
3. Detergent composition according to claim 1, in which the calcium complexing compound is ethane hydroxy diphosphonic acid or its sodium, potassium or ammonium salt.
4. Detergent composition according to claim 1, in which the calcium complexing compound is a poly-alpha-oxyacrylic acid or its sodium, potassium or ammonium salt, having a minimum molecular weight of 261 and carboxylic group/hydroxyl group ratio of 1:2 to 3:1.
5. Detergent composition according to claim 4, in which the carboxylic group/hydroxyl group ratio is 1:1.
6. Detergent composition according to claim 1, in which the calcium complexing agent is a mixture of ethane diamino tetramethylene phosphonic acid and poly-alpha-oxyacrylic acid in a weight ratio of 1:5 to 1:2.
7. Detergent composition according to any one of claims 1—6, in which the protective colloid is gelatin.
8. Detergent composition according to any one of claims 1—6, in which the protective colloid is gelatin.
9. Detergent composition according to any one of claims 1—6, in which the protective colloid is polyvinylpyrrolidone with a K-value of between 15 and 30 and an average molecular weight of between 10,000 and 40,000.
10. Detergent composition according to any one of claims 1—9, in which the phosphate builder salt content is 15—30% by weight.
11. A detergent composition according to any one of claims 1—10, substantially as described in the Examples.
12. A detergent composition according to claim 1 substantially as herein described.

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